

**Novel Polymeric Materials with Superior Mechanical Properties via Ionic Interactions**

**Final Progress Report**

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## A Statement of the Problem Studied

The overall aim of our project is to develop novel polymeric materials with superior mechanical properties, which can be achieved through incorporation of ionic groups (bonds). One way of achieving this goal is to incorporate ionic groups (ionic bonds) into a *liquid crystalline polymer* (LCP), which can lead to a significant increase in mechanical properties (especially in compressive load). Another way of developing novel materials is to blend ionic LCP with a polar polymer, typically used as an engineering polymer, which can lead to significant enhancement in mechanical properties of the parent polymer.

## A Summary of the Most Important Results

Since technical materials were reported in the interim progress reports, only a summary of the most important results are given. We have developed novel ionic LCPs that show enhanced mechanical properties (especially in compressive strength) and compatibility with other polymers. A base polymer of ionic LCPs is a wholly aromatic polyester, better known as *Vectra* of Hoechst-Celanese. To the best of our knowledge, this is the first successful demonstration of improved compressive properties via introduction of ionic bonds.

### 1. Development and Mechanical Properties of Ionic LCP with meta-linked 5-sulfoisophthalate (SI) units

We have found that tensile properties of LCP films can be enhanced significantly; e.g., upon addition of only 1 mol% ionic groups (Ca salt) into Vectra, the modulus increases from 13 to 42 GPa (3.2 times increase) and the tensile strength increases from 142 to 477 MPa (3.4 times increase), while the elongation at break is little changed. We believe that this increase in the strength arises from an increase in shear strength due to increased intermolecular interactions via *ionic bonds*.

More importantly, compressive properties are found to be enhanced. One of the inherent problems of LCPs is their poor compressive (and transverse) strength in contrast to high longitudinal strength. We have found for the first time that the introduction of ionic groups (or bonds) into Vectra leads to enhanced compressive properties. Observation of specimens of (1) knotted fibers in the form of a single loop and (2) fibers embedded in a matrix of a composite that is under compressive load, can provide information on the compressive strength. For example, when subjected to compressive load, nonionic Vectra fibers (embedded in a matrix polymer) show *kink bands* under compressive load of 300 lb, while ionic Vectra fibers (1mol%; Na salt) show no kink bands under the same conditions. Kink bands are deformation mechanism of high-performance fibers which develop due to a low compressive strength. When the shear strength across planes containing molecules is low, kink bands are formed rather easily. Our results suggest that the compressive properties of Vectra are enhanced through introduction of ionic bonds. This is because the weak lateral cohesion between Vectra molecules are enhanced by such strong ionic bonds. It is of interest to note that introduction of covalent cross-links in liquid crystalline polymers has led to little success in improvement of compressive strength. This contrast is due to the *nondirectional nature of ionic bonds* in contrast to the directional nature of covalent bonds; nondirectional bonds seem to better serve to enhance compressive properties.

## 2. Development and Mechanical Properties of Novel ionic LCP with para-linked hydroquinone-2,5-disulfonate (HQDS) units

Following the first work on ionic Vectra that contains meta-linked “kinked” units, *5-sulfoisophthalate (SI)*, we have developed a new type of ionic Vectra, which contains para-linked “straight” units, *hydroquinone-2,5-disulfonate (HQDS)*.

Like ionic Vectra with SI units, ionic Vectra with HQDS units show nematic liquid crystalline structure. Thermal (DSC) analysis on ionic Vectra containing *HQDS (K salt) units* shows an interesting trend: the nearly constant melting temperature,  $T_m$ , and crystallization temperature,  $T_c$ , against ionic content. This is in marked contrast to the results on ionic Vectra containing SI units, where both  $T_m$  and  $T_c$  decrease with ionic content. This is because the ionic Vectra with HQDS units contains ionic monomer with “straight” units, which do not disturb the semi-rigid chain structure of Vectra, whereas the ionic Vectra with SI units contains ionic monomer with “kinked” units, which decrease the rigidity of the backbone chains. The loss of rigidity leads to lower  $T_m$  and  $T_c$ .

We have found that the tensile properties of this new ionic Vectra increase with increasing ionic content, e.g., the tensile strength increases from 142 MPa for nonionic Vectra to 364 MPa for 4 mol% ionic Vectra. This increase in tensile strength is more significant than that for the ionic Vectra with SI units. Again, this is due to the incorporation of “straight” units into Vectra molecules.

## 3. Simple modeling (for extrusion and tension/compression)

We have proposed a simple model that can explain the enhancement in the mechanical properties of ionic Vectra. The basic idea of the model is that the enhancement in intermolecular interactions through ionic bonds should be the most important factor for the significant enhancement in the mechanical properties.

First, a model of extrusion of ionic Vectra is given: during film/fiber formation through melt extrusion, the ionic cross-links may be broken (or weakened) on melting at high temperatures and reformed after chain alignment by elongational flow during extrusion. The highly aligned polymer chains and ionic cross-links can be “frozen in” when the film is quenched in air.

Second, a model of mechanical behavior of ionic Vectra is given. As we have observed, tensile properties of Vectra are enhanced significantly upon addition of ionic groups. Ionic groups form strong ionic cross-links between the LCP chains, which provide stronger lateral support to the highly aligned macromolecules. This allows higher tensile load being transferred between finite length polymer chains. Unlike covalent cross-links, which usually reduce the tensile properties of the LCP, ionic cross-links enhance tensile properties of the LCP.

Finally, as demonstrated in our experiments on ionic Vectra with SI units, the ionic Vectra shows better compressive properties. Kink bands are deformation mechanism of high-performance fibers which develop due to a low compressive strength. Since chain buckling is needed for kink band formation and since, prior to chain buckling, inter-chain bonds must be broken, the enhancement in

inter-chain bonds hinders kink band formation. In other words, higher compressive stress is needed to produce kink bands. Thus, compressive properties are enhanced for ionic Vectra, since the weak lateral cohesion between molecules are enhanced by the strong ionic bonds. Again, it is of interest to note that another attempt to overcome weak compressive strength, an introduction of covalent cross-links into liquid crystalline polymers, has led to little success in improvement of compressive strength.

#### 4. Formation and Mechanical Properties of Ionic LCP blends (with PET)

The first blend system studied is made of an ionic Vectra and a polar polymer, poly(ethylene terephthalate)(PET). We have found that not only are the modulus and strength enhanced, but also is the ductility. For example, the strain at break increases from 4.1% for PET to 12.5% (3 times) for Blend 1 (3 mol% ionic Vectra/PET (5/95)) and to 16.3% (4 times) for Blend 2 (6 mol% ionic Vectra/PET (5/95)). It is also noted that blends containing ionic Vectra having higher ion content (6 mol% in Blend 2 vs. 3 mol% in Blend 1) shows more a significant increase in mechanical properties. These results arise from good *miscibility/adhesion* between two polymers (ionic Vectra and PET), since ionic groups of ionic Vectra and ionic dipoles of PET can interact strongly through *ion-dipole bonds*.

#### 5. Formation and Mechanical Properties of Ionic LCP blends (with PEN)

The second blend is made of an *ionic Vectra* and a polar polymer, *poly(ethylene 2,6-naphthalate)(PEN)*. In this work, we have kept the content of ionic Vectra to be only 1.5 wt%. We have found that not only is the strength enhanced, but also is the ductility. For example, the tensile strength increases from 86 MPa for PEN to 183 MPa (113 % higher) for the blend. Also, the strain at break increases from 102 % for PEN to 185 % (80 % higher) for the blend and toughness increases from 56 MJ/m<sup>3</sup> for PEN to 186 MJ/m<sup>3</sup> (230 % higher) for the blend. Again, these results arise from good miscibility/adhesion between the two polymers (ionic Vectra and PEN), since ionic groups of ionic Vectra and ionic dipoles of PEN can interact strongly through *ion-dipole bonds*. This is confirmed by scanning electron microscopy (SEM). Ionic Vectra molecules work as a reinforcer for the PEN matrix.

Although we have used PET or PEN as a polar polymer, we can expect that enhancement in mechanical properties will also be observed for other polar polymers when blended with ionic Vectra. This expectation is justified by the fact that *ion-dipole bonds* are found to be useful in enhancing miscibility of various polymer blends in which both components are conventional, flexible polymers. As we have demonstrated, a key to the success of making LCP blends with enhanced mechanical properties is the use of ionic LCP as a component, which leads to enhanced miscibility and adhesion between the component polymers.

#### Overall

We have found and successfully demonstrated for the first time that ionic bonds incorporated into LCPs can overcome inherent weakness of LCPs; i.e., weak compressive strength. Without sacrificing already excellent tensile strength (or even enhancing the strength), we can enhance compressive

strength via introduction of ionic bonds. It should be stressed that only small amounts of ionic groups (typically several mol%) are needed to achieve these results. Coupled with advantage of ionic bonds, such as *thermal processability*, ionic LCP will find various applications and many novel ionic LCPs will be developed based on our finding.

Furthermore, we have clearly demonstrated that LCP can be more miscible with a polar polymer, when ionic groups are added to LCP chains. These blends show enhanced mechanical properties. Since many engineering polymers are polar polymers having ionic dipoles, many polymer blends can be created by mixing ionic LCP with various polar polymers.

#### A List of All Publications

1. "Fatigue Behavior of Sulfonated Polystyrene Ionomers and Their Blends with Polystyrene," *Polymer*, 38, 309-315 (1997), M. Bellinger, J.A. Sauer, and M. Hara.
2. "Effect of Polar and Nonpolar Plasticizers on the Mechanical Properties of a Sulfonated Polystyrene Ionomers," *J. Polym. Sci., Polym. Phys. Ed.*, 35, 1291-1294 (1997), X. Ma, J.A. Sauer, and M. Hara.
3. "Poly(p-phenylene terephthalamide) (PPTA) having ionic and nonionic side groups and their blends with poly (4-vinylpyridine)," *Polymer*, 38, 2773-2780 (1997), G. Parker and M. Hara.
4. "Melt-processable molecular composites via ion-dipole interactions: poly(p-phenylene terephthalamide)(PPTA) anion and poly (vinylpyridine)s," *Polymer*, 38, 2701-2709 (1997), G. Parker and M. Hara.
5. "Poly(methyl methacrylate) Ionomers: 3. Plasticizer Effect," *Polymer*, 38, 4425-4431 (1997), X. Ma, J.A. Sauer, and M. Hara.
6. "Ionic Naphthalene Thermotropic Copolymers: Effect of Ion Content," *Macromolecules*, 30, 3803-3812 (1997), Y. Xue and M. Hara.
7. "Blends made of Ionomer and Ionomer Precursor Polymer," in "Morphological Control in Multiphase Polymer Mixtures", R.M. Briber, C.C. Han, and D.G. Peiffer ed., MRS Symposium Series, 461, 19-24 (1997), with M. Bellinger, X. Ma, L. Tsou, J.A. Sauer, and M. Hara.
8. "Mechanical Properties of Ionomers and Ionomer Blends," in "Encyclopedia of Polymer Processing Technology", N.P. Cheremisinoff ed., Marcel Dekker, New York, 145-153 (1997) M. Hara and J.A. Sauer.
9. "Effects of Ionic Interactions on Mechanical Properties of Polymers and Polymer Blends/Composites," *Proceedings of 10th International Conference on Deformation, Yield, and Fracture of Polymers*, p.133-136 (1997), X. Ma, J.A. Sauer, G. Parker, W. Chen, L. Tsou, and Y. Xue, and M. Hara.
10. "Synergism in Mechanical Properties of Polymer/Polymer Blends," *J. Macromol. Sci., Rev. Macromol. Chem. Phys.*, C38(2), 325-360 (1998), M. Hara and J.A. Sauer.

11. "Blends of Poly(methyl methacrylate)(PMMA) with PMMA Ionomers: Mechanical Properties," *J. Polym. Sci., Polym. Phys. Ed.*, 36, 1235-1245 (1998), with L. Tsou, X. Ma, and J.A. Sauer.
12. "Ionomer Blends: Morphology and Mechanical Properties," *Korean J. Chem. Eng.*, (invited featured article), 15, 353-361 (1998), with J.A. Sauer.
13. "Ionic Naphthalene Thermotropic Copolymers: Divalent Salts and Tensile Mechanical Properties," *Macromolecules*, 15, 7806-7813 (1998), with Y. Xue and H. Yoon.
14. "Interfacial Bonding between Glass Fibers and Ionomer Matrix," *J. Polym. Sci., Polym. Phys. Ed.*, 37, 2705-2710 (1999), with D. Elley-Bristow, M. Bellinger, and J.A. Sauer.
15. "Mechanical Properties of Molecular Composites: 1. Poly(p-phenylene terephthalamide) Anion Molecules Dispersed in Poly(4-vinylpyridine)" *J. Polym. Sci., Polym. Phys. Ed.*, 37, 2201-2209 (1999), with J.A. Sauer and L. Tsou.
16. "Mechanical Properties of Molecular Composites: PPTA Anion Molecules dispersed in Poly(ethylene oxide) (PEO)," *J. Polym. Sci., Polym. Phys. Ed.*, in press, with J.A. Sauer and L. Tsou.
17. "Molecular Composites of Poly(p-phenylene terephthalamide) Anion and Poly(ethylene oxide): Thermal Behavior and Morphology," *J. Polym. Sci., Polym. Phys. Ed.*, in press, with J.A. Sauer and L. Tsou.
18. "Molecular Composites of Poly(p-phenylene terephthalamide) Anion and Poly(propylene oxide) : Mechanical Properties," *Polymer*, in press, with J.A. Sauer and L. Tsou.
19. "Ionic Naphthalene Thermotropic Copolymers: Enhancement in Compressive Properties," *Macromolecules, submitted*, with Y. Xue and H. Yoon.
20. "Novel Blends Based on Ion-Containing Thermotropic Liquid Crystalline Polyester and Poly(ethylene terephthalate)," *Polymer*, Submitted, with Y. Xue.

A List of All Participating Scientific Personnel

Dr. Masanori Hara  
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Li-Chun Tsou (earned Ph.D. degree during the period)  
Weng-Chao Chen (earned Ph.D. degree during the period)

## Technology Transfer

Contacts with the following institutions were made. Names and telephone numbers of the people contacted are shown.

- Army Laboratories, Picatinny Arsenal: Dr. D. Wiegand, (201) 724-3336
- Hoechst-Celanese: Dr. H.H. Yoon (732) 522-7786

Our work has been presented at various meetings and organizations. A list of presentations is shown below:

1. "Polymer Blends made of Ionomer and Ionomer Precursor Polymer," at MRS meeting, Boston, Dec. 1996.
2. "Effects of Ionic Interactions on Mechanical Properties of Polymers and Polymer Blends/Composites," at 10th International Conference on Deformation, Yield, and Fracture of Polymers, Cambridge, England, April, 1997.
3. "Effects of Ionic Interactions on Mechanical Properties of Polymers and Polymer Blends/Composites," at Kyoto University, Japan, February, 1998.
4. "Effects of Ionic Interactions on Mechanical Properties of Polymers and Polymer Blends/Composites," at Osaka Prefecture University, Japan, February, 1998.
5. "Ion-Containing Polymeric Materials," at Fukui University, Japan, February, 1998.
6. "Effects of Ionic Bonds on Physical Properties of Polymeric Materials," Kyushu University, Japan, March, 1998.
7. "Effects of Ionic Bonds on the Properties of Polymers," Rengo, Japan, June, 1998.
8. "Effects of Ionic Bonds in Polymeric Materials," Sony, July, 1998.
9. ""Ionic Main-Chain Thermotropic Liquid Crystalline Polymers (TLCPs)" at the American Physical Society Meeting, Atlanta, March, 1999.
10. "Deformation Behavior and Mechanical Properties of Polymer Blends via Ionic Cross-links" at the American Physical Society Meeting, Atlanta, March, 1999.

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